

THERMODYNAMIC STABILITY OF NANODIAMONDS: A NANOTHERMODYNAMIC APPROACH

H. Cui, C. X. Wang, P. Liu, G. W. Yang

State key laboratory of optoelectronic materials and technologies, School of Physics Science & Engineering,
Zhongshan University, Guangzhou 510275, P. R. China

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Abstract

Since Lewis *et al.* found nanometer-scaled diamonds from primitive meteorites in 1987, a lot of researchers have also detected nanodiamonds in protoplanetary nebulae, interplanetary dust originating from comets and asteroids, and some circumstellar disks. All extraterrestrial nanodiamonds have similar size distribution, i.e., 3-5 nm, so far. On the Earth, nanodiamonds synthesize by detonation, chemical vapor deposition (CVD), and hydrothermal synthesis and reduction of carbide (HSRC). Pure TNT detonation synthesizes nanodiamonds with diameters about 10 nm. However, Chen *et al.* synthesized mostly spheroidal diamond nanoparticles with sizes of 3-6 nm by detonating TNT in the inert gases atmosphere. Similarly, nanodiamonds have been produced using CVD techniques. Lee *et al.* found diamond nanoparticles with diameter of 2-6 nm (small enough to identify the nucleation sites) in CVD diamond films. Furthermore, Gruen *et al.*, by partially or outright replacing the hydrogen with argon in the CVD process, deposited the smooth films of nanoparticles only a few nanometers in size. Recently, the important progress of micron-sized diamond synthesis was developed by HSRC with hydrogen or without hydrogen under conditions of pressure less than 200 MPa and temperature not exceeding 1300 K. Importantly, Gogotsi *et al.* realized the conversion of silicon carbide to diamonds with diameter of about 5 nm in the noble gas atmosphere under ambient pressure and temperature less than 1300 K conditions. Thus, both extraterrestrial and Earth's nanodiamonds are not only stable, not also have the nearly equal size distribution. These important data imply that there would be a common underlying factor in the formation of nanocrystalline diamonds. To our best knowledge, a few studies are involved in the stability of nanodiamonds. However, in all these calculations and experiments mentioned above, we hardly find the reasonable and satisfying explanation for the two fundamental issues: which physical origin causes the nanodiamond stability and why the nearly equal size distribution of nanodiamonds produced in space and on the Earth under very different temperature-pressure conditions is in the range of 3-5 nm. To gain a better understanding of the physical origin of the two fundamental issues mentioned above from the point of view of thermodynamics, in this study, we therefore perform the phase stability analysis of nanodiamonds and calculations of the critical nuclei sizes of diamonds upon CVD and HSRC systems. Interestingly, our theoretical results show that the radiuses of critical nuclei of diamonds upon CVD and HSRC are less than 2.5 and 3.0 nm, respectively. Furthermore, our analysis indicate that at atmospheric pressure and temperature not exceeding 1300 K, nanodiamonds less than 6 nm in diameter are thermodynamic stable phase. Additionally, we provide a reasonable explain for the diamond nucleation upon the hydrogen-free CVD.